Fabrication of Sr-Doped LaFeO₃ YSZ Composite Cathodes

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Composites of yttria-stabilized zirconia (YSZ) with Sr-doped LaFeO₃ (LSF) were studied for application as high-performance cathodes for solid oxide fuel cells (SOFCs). The composites were formed by aqueous impregnation of porous YSZ with La, Sr, and Fe salts, followed by calcination at various temperatures. X-ray diffraction measurements showed that the LSF perovskite phase had formed by 1023 K and that solid-state reaction with the YSZ did not occur below approximately 1223 K. The electronic conductivity of the 40 wt % LSF-YSZ composite was maximized by calcination at 1123 K. SOFCs prepared with a 40 wt % LSF-YSZ cathode showed improved performance over SOFCs prepared with conventional LSM-YSZ cathodes at 973 K, although the performance of cells made with cathodes having lower LSF content did not perform as well. Based on measurements with a reference electrode on an electrolyte-supported cell, the impedance of the 40 wt % LSF-YSZ cathode is approximately 0.1 ohm cm² in air at 973 K. Finally, a cathode-supported cell was fabricated from a 40 wt % LSF-YSZ cathode and shown to perform well in H₂.
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The cathodes in solid-oxide fuel cells (SOFCs) are typically made from a composite of an electronically conductive oxide with the electrolyte oxide. For example, the conventional cathode material for cells made with yttria-stabilized zirconia (YSZ) electrolytes is a mixture of YSZ and Sr-doped LaMnO₃ (LSM).[1] The importance of having the YSZ in the electrode is that it enhances ionic conductivity, thereby increasing the electrochemically active region within the electrode. A number of groups have shown that YSZ particles within the cathode provide "channels" for the conduction of oxygen ions.[2,3] These groups have also demonstrated the importance of having a sufficiently high sintering temperature for the cathode so that the YSZ in the cathode is attached to the electrolyte so as to allow transport of ions into the electrode. Unfortunately, high-temperature calcination can result in a solid-state reaction between the oxides making up the electrode. Therefore, the sintering temperature for the composite cathodes must be a compromise, high enough to allow sintering of the YSZ phase to the electrolyte but low enough to prevent the solid-state reactions.

In the case of LSM-YSZ composites, this compromise is possible. The formation of the insulating La₂Zr₂O₇ phase does not begin below approximately 1523 K,[4] a temperature sufficiently high to allow sintering of the YSZ phase. However, with some other conducting oxides, the solid-state reaction begins at temperatures that are too low to allow YSZ sintering. This is the case for Sr-doped LaFeO₃ (LSF) and LaCoO₃ (LSCo), two oxides which exhibit superior performance as SOFC cathodes compared to LSM.[5-8] In order to use these oxides in YSZ-based cells, it is usually necessary to avoid contact with the YSZ by incorporating an additional material, such as Gd-doped ceria, between the cathode and the electrolyte as a barrier.[7,8]

In our laboratory, we have been developing low-temperature methods for preparing composite anodes so that we can replace Ni as the metallic component with coke-resistant Cu.[9-13] Our approach has been to synthesize a highly porous YSZ that has been calcined to high temperatures together with the electrolyte and then to add the active components for the electrode impregnation of the porous YSZ with soluble salts. This approach allows a separate calcination temperature for YSZ and the other components of the electrode. The approach also provides a structure that is quite different from composites prepared using more conventional methods in that the active components in the electrode can coat the surface of the preformed YSZ structure.[12]

In this paper we demonstrate that it is possible to prepare an LSF-YSZ composite that provides high performance as the cathode for an SOFC, without use of a barrier layer, using impregnation methods for preparing the LSF. Furthermore, because the structural component in the cathode is YSZ, there is a sufficiently good match in the thermal expansion coefficients of the electrolyte and the composite cathode such that cathode-supported SOFCs can be prepared using this method.

Experimental

The LSF-YSZ composites in this study were fabricated by impregnation of a porous YSZ matrix with aqueous solutions containing La, Sr, and Fe salts. The solutions were prepared by dissolving the nitrate salts [La(NO₃)₃·6H₂O, Alfa Aesar, ACS 99.9%; Sr(NO₃)₂, Alfa Aesar, ACS 99.0%; and Fe(NO₃)₃·9H₂O, Alfa Aesar, ACS 98 + %] in water at a molar ratio of La:Sr:Fe = 0.8:0.2:1. After adding citric acid to the point at which the concentration of citrate ions was equal to that of the metal ions, the clear mixture was stirred for 24 h at 333 K, with water added to make up for that lost by evaporation. The citrate complexes were highly soluble in water but it was necessary to maintain a low concentration, 1.0 mol of metal ions per liter, to avoid having high viscosities.[14] In order to introduce a sufficient amount of LSF into the YSZ, it was usually necessary to use multiple impregnations and to calcine the impregnated salts to 723 K to remove the citrate and nitrate ions between impregnations.

The porous YSZ matrices were fabricated using procedures described in more detail elsewhere.[12,15] The YSZ powder (18.2 g, 8-YSZ, Tosoh Corp., TZ-8Y) was mixed with 30 g of distilled water, a dispersant (1.27 g, Duramax 3005, Rohm & Haas), binders (3.85 g HA12 and 5.73 g B1000, Rohm & Haas), and pore formers [18.3 g of either graphite (GE, Alfa Aesar, 325 mesh, conductivity grade) or a mixture of graphite and polymethyl methacrylate (PMMA; Scientific Polymer Products, Inc., Mw 540,000)]; then the resulting slurry was cast into the desired shape. After calcination to 1823 K, the YSZ was found to have porosities between 60 and 70%, depending on the PMMA:graphite ratio, as shown by the weight change of the sample after water immersion.[12,15] (Note: It has been shown previously that addition of PMMA results in relatively large, ~40 μm, spherical pores which were found to aid in the impregnation of salts.[15]) The phase and microstructure of selected samples were investigated using Cu Kα X-ray diffraction (XRD) and scanning electron microscopy (SEM; JEOL JSM-6300LV).

For measuring electrical conductivities, the YSZ, 60% porous (PMMA:graphite = 0), was formed into rectangular pieces, 2 × 2 × 10 mm. After addition of LSF, the electrical conductivities were determined using the standard four-probe dc method. The samples were placed in a holder, and external platinum foils were

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attached to both ends. Current from a Tektronix PS 280 dc power supply was passed through the samples while monitoring the voltage across the samples. All conductivities were measured in air.

The initial step in preparing the anode-supported fuel cells involved casting a two-layer green tape in which a tape with pore formers (PMMA:graphite = 1.35) was cast over a tape without pore formers, the same as described in previous papers.[10,12,15] The targeted thicknesses for the porous and dense YSZ layers were 600 and 100 μm, respectively. To provide a porous YSZ matrix for the cathode, a YSZ slurry having a composition similar to the tape with pore formers was painted onto the green two-layer tape on the side without pore formers. The targeted thickness of the cathode layers was 60 μm and the PMMA:graphite ratio for this slurry was 0. After firing this three-layer tape to 1823 K, the LSF-citrate solution was impregnated into the cathode YSZ matrix and calcined in air to 1123 K, after which the Cu (20 wt %) and ceria (10 wt %) were added to the opposite side by impregnation with nitrate salts, followed by calcination in air to 723 K.

In order to compare the LSF-YSZ composite cathodes to conventional LSM-YSZ cathodes, one anode-supported cell was prepared with LSF-YSZ over half the area of the air electrode and LSM-YSZ over the other half. The distance between the two cathodes was about 1 mm. The LSM-YSZ electrode was attached to the dense side of the YSZ bilayer after high-temperature calcination. The LSM-YSZ was prepared from 50 wt % YSZ and LSM ($La_{0.8}Sr_{0.2}MnO_3$, Praxair Surface Technologies) mixture, with 10 wt % graphite as a pore former, applied to the dense YSZ side of the ceramic wafer as a paste, and calcined in air at 1523 K.[12]

Several cathode-supported cells were fabricated from three-layer tapes similar to that used to make the anode-supported cells, with the only exceptions being that the LSF was impregnated into the 600 μm porous layer and the PMMA:graphite ratio used in making the 60 μm layer used for the anode was 0.74.

Finally, an electrolyte-supported cell was made with a reference electrode in an attempt to separate cathode and anode losses. Small (final size of ~0.35 cm² area, 60 μm as cathode matrix and 600 μm as anode matrix), circular pieces were cut from a green YSZ tape made with pore formers. These were laminated onto opposite sides of a thick green tape that had no pore formers (final thickness 700 μm), using care to position the pieces in exact alignment with each other.[16-18] (That good alignment of the electrodes was achieved by the fact that ohmic contribution to the reference-to-cathode and reference-to-anode impedance spectra were essentially the same.[16,17]) After calcination of the green tape, the electrodes were prepared as described previously, with the cathode having 40 wt % LSF. The reference electrode was made from Pt paste and was attached on the cathode side at a distance from the cathode that was well over three times the electrolyte thickness.

For the fuel-cell measurements on the electrode-supported cells, the electrode area opposite the thicker support electrode was 0.33 cm². Electronic contacts were made using Ag mesh with Ag paste at the cathode and a Au wire with Au paste on the anode. Each cell was sealed onto a 1.0 cm alumina tube using a ceramic adhesive (Aremco, Ultra-Temp 516). The entire cell was placed inside a furnace and heated to 973 K at 2 K/min. Before making measurements in hydrogen, the anodes were exposed to n-butane fuel for 20 min to activate the cells, as discussed elsewhere.[19] Dry H_2 was then fed to the anode at a flow rate of 100 mL/min, while the cathode was simply left open to air.

All the impedance data were recorded in the galvanostatic mode using a Gamry Instruments potentiostat, with a frequency range from 0.01 Hz to 100 kHz and amplitude of 3 mA/cm². Unless otherwise noted, the data shown in this paper were taken at a dc current density of 300 mA/cm²; however, impedance curves taken at other current densities were essentially indistinguishable, as expected based on the fact that the V-I curves in this study were always linear. The two-electrode impedance curves were measured using the cathode as the working electrode and the anode as the counter and reference electrodes. On the electrolyte-supported cell, cathode imped-
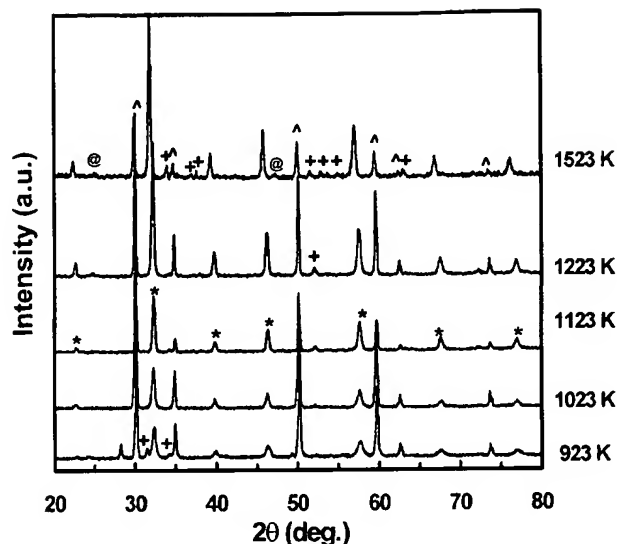

Figure 1. XRD patterns of the LSF-YSZ composite, prepared by impregnation, following various calcination temperatures. The various phases are marked (*) LSF, (∧) YSZ, (+) Fe-O, and (@) $La_2Zr_2O_7$.

ance results were obtained using a three-electrode technique with the cathode as the working electrode, the reference electrode as the reference, and the anode as the counter electrode. Anode results were recorded with the counter and working electrodes reversed.

Results

In order to achieve a high-performance cathode from an oxide made from Sr, La, and Fe, it is necessary that these form the perovskite structure and that no insulating phases, such as $La_2Zr_2O_7$, are formed. Therefore, we used XRD to examine the structure of composites formed after the addition of 40 wt % of an oxide having the composition of LSF to porous YSZ, as a function of calcination temperature, with the result shown in Fig. 1. Peaks corresponding to the LSF perovskite phase (notably, those peaks at 23, 32, 40, 46, 57, 67, and 77° 2θ) are clearly apparent at 1023 K and become sharper after calcination above 1123 K. However, new peaks at 34, 37, 51, 53, and 64°, associated with Fe-O compounds, appear to be present in trace amounts in all the patterns and grow in intensity after calcination above 1223 K. Peaks at 28 and 47° 2θ, associated with $La_2Zr_2O_7$, are clearly present in the pattern at 1523 K.

Because electronic conductivity in an SOFC electrode is crucial, conductivity measurements were performed on LSF-YSZ samples at 973 K, with the results shown in Fig. 2. Figure 2a shows the conductivity of samples with 40 wt % LSF as a function of calcination temperature. The data show that there is a dramatic increase in the conductivity of the composite after increasing the calcination temperature from 973 to 1123 K, the same temperature range in which the perovskite phase is formed. Heating to higher temperatures causes the conductivity to decrease. The absolute value of the conductivity after calcination at 1123 K, ~1.3 S/cm, is about 30 times lower than one would expect for pure, dense LSF;[20] however, it is comparable to what we measured for 50 wt % LSM-YSZ composites that we prepared by conventional methods.[21] Figure 2b shows the effect of composition on the conductivity of the LSF-YSZ composites that had been calcined to 1123 K. As reported earlier for composites prepared by impregnation of a conducting material into YSZ,[21] the samples prepared by impregnation show reasonably high conductivities at relatively low weight fractions of LSF. This is almost certainly due to the nonrandom structure of the impregnated composites in which the LSF coats walls of the YSZ matrix.
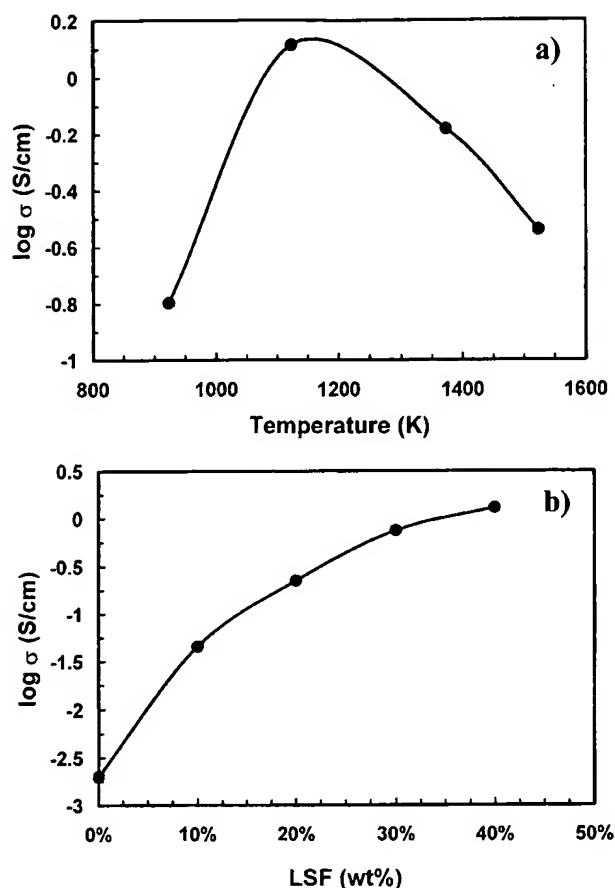
Figure 2. Electrical conductivities of LSF-YSZ composites at 973 K as a function of (a) calcination temperature with 40 wt % LSF and (b) content after calcination at 1123 K.

Figure 3. SEM images of (a) the initial YSZ matrix and (b) the LSF-YSZ composite prepared by impregnation.

This nonrandom structure is observable in the SEM micrographs of Fig. 3, where the porous YSZ is shown before (a) and after (b) addition of 40 wt % LSF calcined at 1123 K. The SEM micrographs indicate that the YSZ has relatively uniform pores, $\sim$1–2 μm. After impregnation, 0.2 μm LSF particles are observed coating the YSZ walls.

The performance of cells in dry H_2 at 973 K, made with impregnated LSF-YSZ cathodes, is shown as a function of LSF content in Fig. 4. The composite cathodes in each cell were 60 μm thick and were calcined to 1123 K; the anodes were 600 μm thick, consisting of 20 wt % Cu and 10 wt % ceria; the electrolytes were 100 μm thick. The V-I curves in Fig. 4a demonstrate that the performance increases with the amount of LSF added. Each of the cells showed a reasonable open-circuit voltage (OCV), above 1.15 V, but the maximum power density increased from 150 to 180 and 240 mW/cm^2 as the LSF content increased from 20 to 30 and 40 wt %, respectively. The corresponding two-electrode impedance curves at 300 mA/cm^2 are shown for each of the three cells in Fig. 4b. The most notable change with increasing LSF content is in the ohmic impedance, which decreases from $\sim$1.0 Ω cm^2 for the 20 wt % LSF cathode to $\sim$0.6 Ω cm^2 for the 40 wt % LSF cathode. Based on the reported conductivity of YSZ at 973 K (0.021 S/cm),[22] we estimate that the contribution of the electrolyte to the ohmic impedance is $\sim$0.48 Ω cm^2. An additional 0.1 Ω cm^2 can be attributed to the leads in our system, implying that the ohmic contribution of the 40 wt % LSF-YSZ cathode is probably negligible. Finally, the polarization resistance also decreases, from $\sim$1.0 Ω cm^2 for the low LSF content to $\sim$0.6 Ω cm^2 for the highest LSF content.

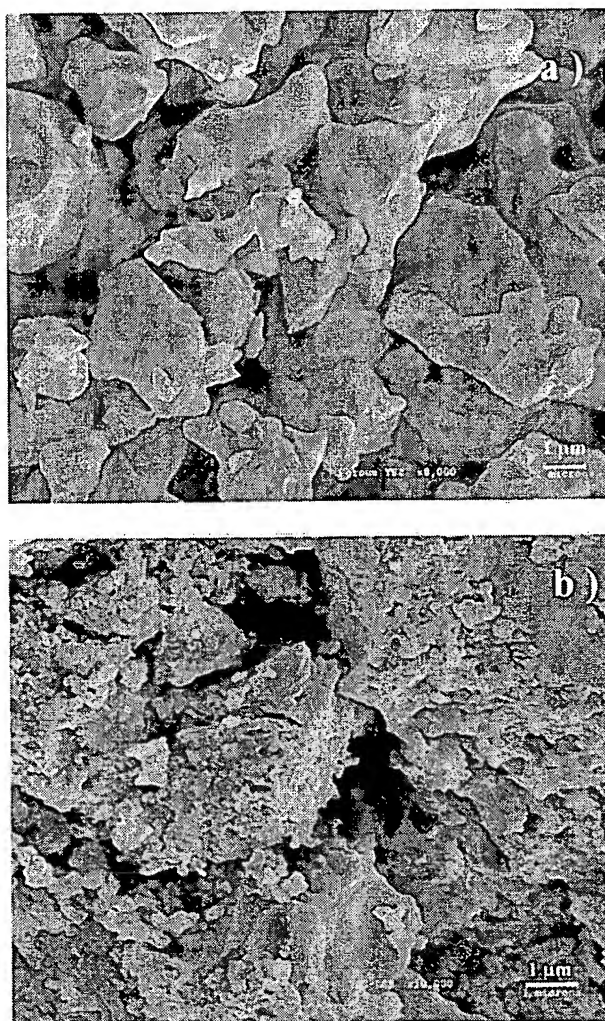In order to get a direct comparison of an impregnated LSF-YSZ cathode with conventional LSM-YSZ electrodes that we used in previous studies, we examined an anode-supported electrolyte having two cathodes, half of the cathode area being covered by a 50 wt % LSM-YSZ electrode and the other half covered by a 40 wt % LSF-YSZ electrode prepared by impregnation. The anode and electrolyte were similar to those used for the results in Fig. 4. As demonstrated in Fig. 5a, the performance of the LSF-YSZ electrode is better than that of the conventional cathode, increasing the maximum power density at 973 K in H_2 from 210 to 230 mW/cm^2. For both cathodes, the V-I curves are also linear over the entire range of current densities. The effect of changing cathode is more easily seen from the two-electrode impedance curves in Fig. 5b. The ohmic contribution to both the LSF and LSM sides of the cell are the same, $\sim$0.6 Ω cm^2, in agreement with our earlier observation that the cathode does not contribute to the ohmic resistance. The primary difference in the impedance curves for the two cathodes is that there is a 2 kHz arc on the part of the cell with the LSM-YSZ cathode that is not present on that part of the cell with the LSF-YSZ cathode. Indeed, this 2 kHz arc has been associated with cathode losses in previous studies of cells with LSM-YSZ cathodes prepared in the manner used in this study.[16,21] The absence of this arc in the LSF-
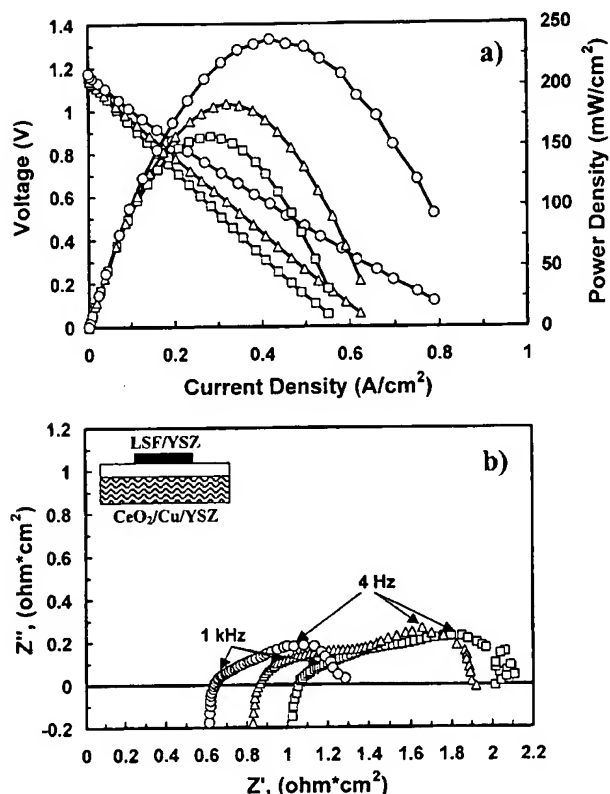
Figure 4. (a) Performance curves in dry H_2 at 973 K with different contents of LSF anode-supported cells. (b) Impedance curves in dry H_2 at 973 K with different contents of LSF in anode-supported cells. (□) 20, (△) 30, and (○) 40 wt % LSF.

Figure 5. (a) Performance curves in dry H_2 at 973 K for the split cell with LSF-YSZ composite prepared by impregnation as a half cathode and LSM-YSZ composite painted as another half in anode-supported cells. (b) Impedance curves in dry H_2 at 973 K for split cell with impregnated LSF as a half cathode and painted LSM as another half in anode-supported cells. (□) 50 wt % LSM and (△) 40 wt % LSF.

YSZ part of the cell provides further evidence that the 2 kHz arc is cathode related.

The results from the cell with the split cathode demonstrate that the performance of the LSF-YSZ electrode is better than that of the conventional LSM-YSZ cathode; however, it is difficult to estimate absolute losses from this kind of measurement. To determine the impedance of the LSF-YSZ cathode, we examined the electrolyte-supported cell that had a reference electrode. As noted in the Experimental section, the electrolyte in this cell was 700 μm thick and great care was taken to ensure that the cathode and anode were symmetrically placed so as to avoid the complications associated with overlap of the working electrodes.[16-18] Figure 6 shows the three-electrode impedance spectra for the cathode and anode on this sample at 973 K, in H_2 with 3% H_2O, at open circuit. The fact that the ohmic contribution is evenly divided between cathode and anode (2.1 Ω cm^2 for the cathode and 2.4 Ω cm^2 for the anode) provides confidence that the anode and cathode contributions are reasonably well separated.[16,17] Even with this split, the inductive tail observed at low frequencies in the cathode spectrum indicates that the anode may be contributing to the cathode spectrum due to the widely different time constants associated with the two electrodes.[16,17] The spectra in Fig. 6 imply that the impedance of the anode is approximately 0.7 Ω cm^2 and that of the cathode is 0.1 Ω cm^2, based on the high- and low-frequency intercepts for the two curves. The value for the Cu-based anode is in reasonable agreement with the value obtained in a previous study for cells prepared in a similar manner, as is the characteristic frequency of the anode arc, ~4 Hz.[16] The characteristic frequency of the LSF-YSZ cathode, 1 kHz, is also similar to that observed for an LSM-YSZ cathode, suggesting that similar processes are associated with both electrodes.
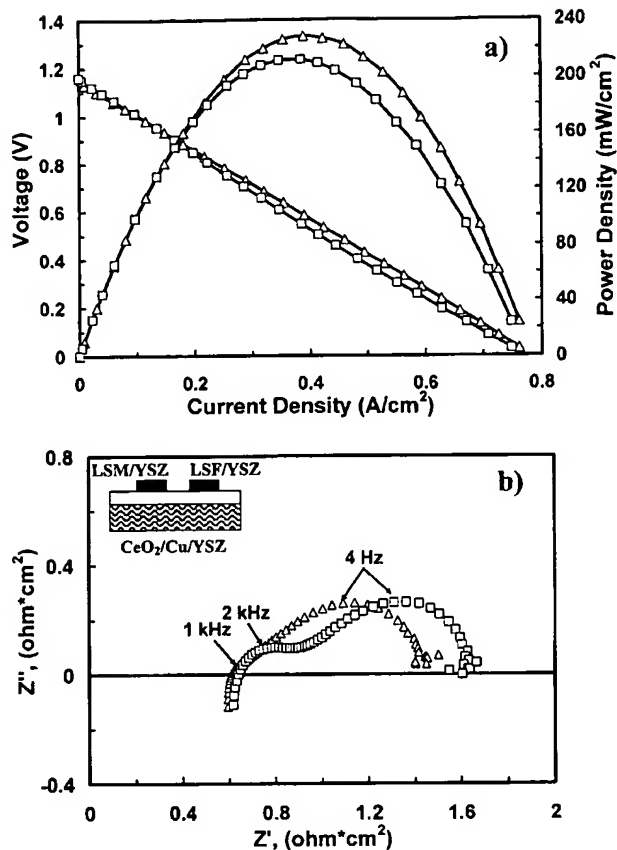
Finally, because the LSF-YSZ cathodes in this study were prepared in a similar manner to that used for preparing the Cu-based, anode-supported cells, it is feasible to prepare cathode-supported
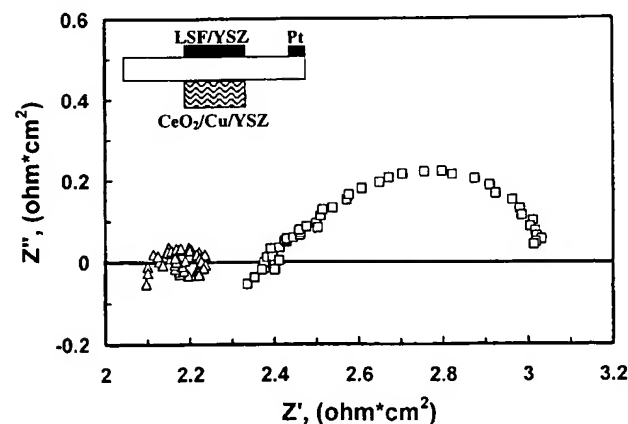

Figure 6. Impedance curves at OCV in humidified H_2 at 973 K for the electrolyte-supported cell having a reference electrode using 40 wt % LSF-YSZ prepared by impregnation as cathode. (□) Anode to reference and (△) cathode to reference.
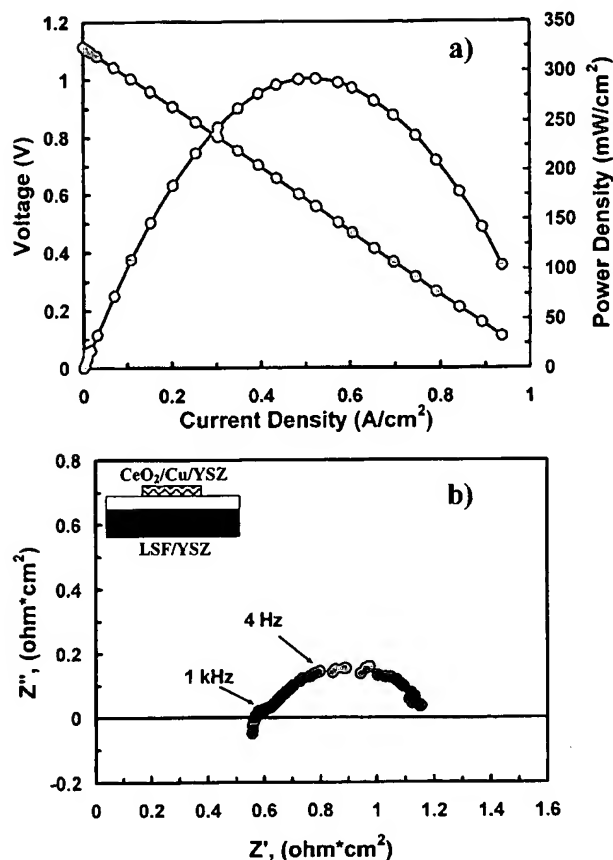
Figure 7. (a) Performance curves of a cathode-supported cell in humidified H_2 at 973 K. (b) Impedance curve of the cathode-supported cell at OCV in humidified H_2 at 973 K.

cells. The cathode-supported cell examined in this study was prepared by impregnating LSF into the 600 μm porous layer, supporting the 100 μm YSZ electrolyte. The anode was attached as described in the Experimental section. The V-I curves in Fig. 7a, obtained in H_2 with 3% H_2O at 973 K, indicate that this cell exhibited even better performance than that of the anode-supported cells, with a maximum power density of 280 mW/cm². The impedance curve in Fig. 7b shows that the ohmic resistance of this cell was less than 0.6 Ω cm². Because the resistance of a 600 μm layer with a conductivity of 1.3 S/cm should be only 0.04 Ω cm², it is reasonable that changing the cathode thickness from 60 to 600 μm should have minimal effect. The total polarization impedance of the electrodes is ~0.7 Ω cm², caused primarily by the anode.

Discussion

The standard material used as the cathode in SOFCs based on YSZ electrolytes continues to be a composite of LSM and YSZ.[1] As pointed out in the Introduction, LSF and LSCo exhibit superior properties to that of LSM, such that there is significant interest in replacing LSM-YSZ composite cathodes with a composite of LSF or LSCo. Because of the tendency of these oxides to react with YSZ at relatively low temperatures, cathodes based on LSF or LSCo are typically formed as a composite with an alternative electrolyte, such as Sm-doped CeO_2 (SDC).[7,8] Cathodes showing high performance can clearly be formed in this way. The work in this paper has demonstrated that there are alternative methods for forming cathodes based on LSF that do not require the inclusion of a third oxide

component. By using low-temperature fabrication methods, LSF-YSZ composites have been formed without any solid-state reaction between the LSF and YSZ.

Based on the reference-electrode measurements, we estimate that the cathode impedance for the LSF-YSZ composites prepared by our methods is approximately 0.1 Ω cm² at 973 K. Given the linearity of the V-I curves, this impedance is also independent of current density over a wide range of values. There is also excellent consistency between this value and earlier estimates from this laboratory of the impedance losses for LSM-YSZ.[16,21] In those earlier studies the cathode resistance for a conventional LSM-YSZ was estimated to be either 0.4 or 0.2 Ω cm², the difference being due to the inclusion of pore formers. In the measurements in the present work on the cell with two cathodes, shown in Fig. 5, the difference between the impedances of the LSF-YSZ and LSM-YSZ is 0.2 Ω cm².

One reason that the LSF-YSZ composites prepared by low-temperature methods show such good performance is likely because of the microstructure in the composite. First, the YSZ within the composite electrode has been calcined to high temperatures so that there should be good connection between the YSZ in the electrolyte and YSZ in the electrode for conduction of ions. Modeling studies have shown that this connection is crucial for obtaining high performance.[2] Second, because LSF is added to a pre-existing YSZ structure in the electrode, the electronically conductive LSF essentially coats the YSZ, providing what is likely to be an optimal three-phase-boundary region. While we did not attempt to optimize the microstructure, it appears that the formation of oxide composites by impregnation of the components of one oxide into a porous matrix of the second oxide presents interesting opportunities for optimization of both composition and microstructure in oxide composites.

An additional advantage to forming the composite by impregnation is that mechanical and thermal-expansion properties of the composite are likely to be that of YSZ, given that YSZ makes up the backbone of the composite. This greatly simplifies the search for materials with matching coefficient of thermal expansion (CTE). The impregnated oxide can be chosen for optimal electronic properties, without the need for changing the composition to adjust the CTE.

The fact that the porous YSZ provides mechanical strength also allows fabrication of cathode-supported electrolytes, as we have demonstrated. Cathode-supported electrolytes allow use of both thin electrolytes and thin anodes. Because gas-phase diffusion can limit performance at high fuel utilization, the use of thin anodes could provide advantages. Furthermore, use of cathode-supported cells frees one to optimize anode performance without requiring that the anode also be the structural component.

In summary, we believe that fabrication of composite oxides by forming a second oxide within the porous electrolyte material offers a number of potential advantages for preparing novel cathode structures and compositions. The work discussed in this paper demonstrates the feasibility of preparing these composites for one particular example; however, similar approaches could be used with different electrolytes and various conducting oxides.

Conclusion

We have shown that it is possible to fabricate composite oxides of YSZ with Sr-doped $LaFeO_3$ (LSF) by impregnation of a porous YSZ matrix with aqueous solutions of Sr, La, and Fe salts. Because the LSF perovskite phase is formed at temperatures below 1123 K, solid-state reactions with YSZ are avoided. The LSF-YSZ composites were shown to exhibit excellent performance as SOFC cathodes (ASR is approximately 0.1 Ω cm² in air at 973 K) and can be made with sufficient strength to allow the fabrication of cathode-supported electrolytes.

Acknowledgments

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